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WADC TECHNICAL REPORT 55-146

ORGANIC DERIVATIVES OF GERMANIUM ORTHO ESTERS OF 2-ALKOXYETHANOLS

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MATERIALS LABORATORY

JUNE 1955

WRIGHT AIR DEVELOPMENT CENTER

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PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
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FOREWORD

This investigation was conducted by the Organic Materials Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center, under Project No. 7340, "Rubber, Plastic, and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", formerly RDO No. 613-15, "Hydraulic Fluids and Lubricants", with Dr. Harold Rosenberg, Mrs. Elizabeth J. Bartholomew, and Lt. Donald F. Kippax acting as project engineers.

The authors wish to express their appreciation to Mr. Richard Sneed, A/1c Ralph Evans, and Mrs. Nora Srp for technical assistance during this investigation, and to Carbide and Carbon Chemicals Corporation for making available some of the 2-alkoxyethanols.

ABSTRACT

An investigation was conducted to determine the applicability of germanium ortho esters, similar to the organosilicates, as base stock materials for high-temperature fluids and lubricants. A series of tetrakis(2-alkoxyethoxy) germanes was synthesized by the reaction of sodium 2-alkoxyethoxides with germanium tetrachloride after it was found that the germanium halide, unlike its silicon analog, failed to react with a 2-alkoxyethanol. Certain of the physical properties of the germanium ortho esters and their resemblance to those of the corresponding silicon derivatives are discussed. In the course of this work a new glycol ether, 2-cyclohexyloxyethanol, was prepared by the action of ethylene chlorohydrin on the sodium salt of cyclohexanol in the presence of xylene.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I. INTRODUCTION (Ref. 1)

In 1948, Abrahamson, Joffee and Post (Ref. 2) reported the synthesis of several tetrakis(2-alkoxy- and 2-aryloxyethoxy) silanes by the reaction of a 2-alkoxy-or 2-aryloxyethanol with tetraethoxysilane. They also noted that when 2-methoxyethanol (Methyl Cellosolve) is treated with silicon tetrachloride, only the tris(2-methoxyethoxy chlorosilane is obtained (in place of the desired tetra-substituted derivative), despite the presence of a large excess of the alcohol. Burkhard (Ref. 3) the same year, however, prepared tetrakis(2-methoxyethoxy) silane by the action of silicon tetrachloride on 2-methoxysilane and claimed the chlorosilane of the former workers to be in reality, identical with the ortho ester. At least one other compound of this type, tetrakis(2-butoxyethoxy) silane, has recently been synthesized and certain of its physical properties determined (Ref. 4).

II. DISCUSSION

In an effort to extend the work on tetrakis(2-alkoxyethoxy) silanes to the germanium series and prepare certain tetrakis(2-alkoxyethoxy) germanes, the reaction of germanium tetrachloride with a 2-alkoxyethanol was first studied in this laboratory. It was found that, contrary to the results obtained with silicon tetrachloride, when 2-methoxyethanol is treated with germanium tetrachloride no reaction occurs. Even after

prolonged heating the alcohol is recovered unchanged upon distillation of the mixture. This observation is not entirely unexpected since Tabern, Orndorff and Dennis (Ref. 5) found that germanium tetrachloride failed to react with boiling ethanol. They and several other workers (Ref. 6 and 7) reported, however, that tetraethoxygermane could be obtained by the reaction of germanium tetrachloride with sodium ethoxide. Later Schwarz and Reinhardt (Ref. 8) synthesized tetraphenoxygermane in a like manner from sodium phenoxide and germanium tetrachloride. Since the start of the present investigation, a paper by Johnson and Fritz (Ref. 9) has been published in which the synthesis of six new tetraalkoxygermanes by the sodium alkoxide method is described. The procedure used by these workers very closely resembles, with only slight modification, that used by the present authors for the preparation of the tetrakis(2-alkoxyethoxy) germanes.

When the sodium salt of a 2-alkoxyethanol, prepared in the presence of a large excess of the alcohol, was treated with germanium tetrachloride, the corresponding tetrakis(2-alkoxyethoxy) germane was obtained. The alcohols used in this study included 2-methoxyethanol (Methyl Cellosolve), 2-ethoxyethanol (Cellosolve), 2-n-butoxyethanol (Butyl Cellosolve), 2-n-hexyloxyethanol, 2-(2-ethylbutoxy) ethanol (2-Ethylbutyl Cellosolve), 2-cyclohexyloxyethanol, and 2-(2-ethylhexyloxy) ethanol (2-Ethylhexyl Cellosolve). The 2-cyclohexyloxyethanol has not

previously been described in the literature and was obtained by the reaction of ethylene chlorohydrin with the sodium salt of cyclohexanol.

The reaction of germanium tetrachloride with the sodium salt of 2-phenoxyethanol gave rise to an amorphous solid which has resisted all attempts at crystallization but is believed to be tetrakis(2-phenoxyethoxy) germane. This observation is in apparent agreement with that made by Post and co-workers (Ref. 2) for the corresponding silicon analog.

The yields and analytical data of the germanium ortho esters prepared in the present study are presented in Table I.

TABLE I

TETRAKIS(2-ALKOXYETHOXY) GERMANES, $Ge(OCH_2CH_2OR)_4$

	R	Emperical Formula	Yield %	Carbon, %[a] Calcd.	Carbon, %[a] Found	Hydrogen, %[a] Calcd.	Hydrogen, %[a] Found
1.	CH_3	$C_{12}H_{28}O_8Ge$	45.4	38.64	38.41	7.57	7.39
2.	C_2H_5	$C_{16}H_{36}O_8Ge$	48.6	44.79	44.79	8.45	8.59
3.	n-C_4H_9	$C_{24}H_{52}O_8Ge$	65.5	53.25	53.37	9.68	9.41
4.	n-C_6H_{13}	$C_{32}H_{68}O_8Ge$	38.7	58.81	58.91	10.48	10.30
5.	$(C_2H_5)_2CHCH_2$[b]	$C_{32}H_{68}O_8Ge$	34.8	58.81	59.31	10.48	10.23
6.	C_6H_{11}[c]	$C_{32}H_{60}O_8Ge$	26.5	59.54	59.42	9.37	9.45
7.	$C_4H_9CH(C_2H_5)CH_2$[d]	$C_{49}H_{84}O_8Ge$	19.9	62.74	62.60	11.06	11.12

[a] Analyses by Analysis and Measurement Branch, Materials Laboratory.
[b] 2-Ethylbutyl. [c] Cyclohexyl. [d] 2-Ethylhexyl.

The yields were lower than those reported for the corresponding tetrakis-(2-alkoxyethoxy) silanes (Ref. 2 and 3) and decreased markedly with the higher molecular-weight alcohols. They were also somewhat lower than those reported for the simple tetraalkoxygermanes (Ref. 9).

Certain of the physical properties, including boiling points, refractive indices, and densities, of the tetrakis(2-alkoxyethoxy) germanes are presented in Table II.

TABLE II

PHYSICAL PROPERTIES OF THE TETRAKIS(2-ALKOXYETHOXY) GERMANES

Compound	B.P. °C.	Mm.	$n^{25}D$	d^{25}_4
$Ge(OCH_2CH_2OCH_3)_4$	111-112	0.05	1.4369	1.2276
$Ge(OCH_2CH_2OC_2H_5)_4$	126-128	0.06	1.4375	1.1510
$Ge(OCH_2CH_2OC_4H_9\text{-}n)_4$	164-169	0.08	1.4399	1.0511
$Ge(OCH_2CH_2OC_6H_{13}\text{-}n)_4$	178-180	0.13	1.4433	1.0092
$Ge\ OCH_2CH_2OCH_2CH(C_2H_5)_2\ _4$	204-206	0.02	1.4457	1.0083
$Ge(OCH_2CH_2OC_6H_{11})_4$[a]	195-197	0.04	1.4468	0.9941
$Ge\ OCH_2CH_2OCH_2CH(C_2H_5)C_4H_9\ _4$	190-193	0.12	1.4486	0.9708

[a] Tetrakis(2-cyclohexyloxyethoxy) germane.

From this table and from Table III, in which are summarized similar physical constants of three silicon analogs, it may be seen that the germanium ortho esters closely resemble the tetrakis(2-alkoxy-

ethoxy) silanes with respect to these physical characteristics. The densities in the present investigation were obtained by means of a pipet-type pychnometer similar to that used by Johnson and Fritz (Ref. 9). The density determinations were made under controlled conditions of low relative humidity to decrease the possibility of hydrolysis taking place.

TABLE III

PHYSICAL PROPERTIES OF SOME TETRA(2-ALKOXYETHOXY) SILANES (Ref. 2,3,4)

Compound	B.P. °C	Mm.	$n^{20}D$	d^{20}_4
$Si(OCH_2CH_2OCH_3)_4$	183	9[a]	1.4213	1.0781
	179-182	10[b]	1.4219	1.0789
$Si(OCH_2CH_2OC_2H_5)_4$	200	9[a]	1.4226	1.0184
$Si(OCH_2CH_2OC_4H_9\text{-}n)_4$	224-226	1[c]	1.4309	0.9603

[a] Data reported by Abrahamson, Joffee and Post
[b] Data reported by Burkhard.
[c] Data reported by Furby.

In Table IV are listed the kinematic viscosities of several tetrakis(2-alkoxyethoxy) germanes and one tetrakis(2-alkoxyethoxy) silane. It may be noted that the viscosity data of the n-butyl germanium derivative closely approximate those of its silicon analog and are in excellent agreement with them in respect to the ASTM slope.

Viscosity measurements were made with standard Ostwald-Cannon-Fenske-type viscosimeters using the oil standard of the American Petroleum Institute.

TABLE IV

VISCOSITY DATA

Compound	Temperature °C	Temperature °F	Kinematic Viscosity, Centistokes	ASTM Slope
$Ge(OCH_2CH_2OCH_3)_4$	-54.0	-65.0	109.8	0.84
	-17.8	0.0	11.6	
	37.8	100.0	2.4	
	98.9	210.0	1.05	
$Ge(OCH_2CH_2OC_2H_5)_4$	-54.0	-65.0	290.3	0.83
	-17.8	0.0	17.6	
	37.8	100.0	3.05	
	98.9	210.0	1.25	
$Ge(OCH_2CH_2OC_4H_9\text{-}\underline{n})_4$	-54.0	-65.0	570.3	0.77
	-17.8	0.0	36.0	
	37.8	100.0	4.6	
	98.9	210.0	1.7	
$Si(OCH_2CH_2OC_4H_9\text{-}\underline{n})_4$	-54.0	-65.0	359.0	0.74
	-40.0	-40.0	104.0	
	37.8	100.0	4.35	
	98.9	210.0	1.67	

In the course of this investigation the infrared absorption spectra of all of the compounds synthesized were obtained. These data will be presented as part of a forthcoming paper on the infrared spectra of germanium ortho esters.

III. EXPERIMENTAL

A. STARTING MATERIALS

The 2-alkoxyethanols, with the exception of 2-n-hexyloxyethanol and 2-cyclohexyloxyethanol, were obtained from Carbide and Carbon Chemicals Corporation and were purified by distillation under reduced pressure after thorough drying over anhydrous magnesium sulfate. Germanium tetrachloride was obtained from the Eagle-Picher Company and was obtained pure by rectification through a Todd Precise Fractionation Assembly.

B. 2-n-HEXYLOXYETHANOL

This alcohol was prepared in 47% yield according to the general method of Cretcher and Pittenger (Ref. 10) by the reaction of ethylene chlorohydrin with sodium n-hexyloxide in excess n-hexanol. The physical properties of the product, b.p. 188-120° (50 mm.), $n^{25}D$ 1.4279, agreed satisfactorily with those previously obtained for the alcohol by other synthetic procedures (Ref. 11 and 12), despite the fact that other workers* could not obtain the alcohol by this method.

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* Cooper and Partridge (Ref. 12) reported that the reaction of ethylene chlorohydrin and sodium n-hexyloxide in boiling xylene failed to yield any product of constant boiling point. The present authors, however, believe this was probably due to their failure to use highly purified n-hexanol for the preparation of the sodium alkoxide.

C. 2-CYCLOHEXYLOXYETHANOL

This heretofore unreported alcohol was prepared by a method similar to that used for the preparation of 2-n-hexyloxyethanol, with the exception that the xylene was used as a solvent for the reaction. Ethylene chlorohydrin was added to the sodium salt of cyclohexanol in the presence of xylene and the mixture refluxed for thirty-six hours. The sodium chloride formed was filtered off and solvent and excess alcohol removed by distillation. Rectification of the residue gave 87.9 g. (60.9%) of 2-cyclohexyloxyethanol, b.p. 90-92° (0.08mm.), $n^{25}D$ 1.4620, d_4^{25} 0.9524.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.47; H, 11.22.

D. TETRAKIS(2-ALKOXYETHOXY)GERMANES

The method for the preparation of this series is illustrated by the preparation of tetrakis(2-ethoxyethoxy) germane.

In a one-liter, three-necked flask equipped with a mercury-sealed Hershberg stirrer, a Friedrichs condenser, and a dropping funnel was placed 388 ml. (360.5 g., 4.0 moles) of freshly distilled 2-ethoxyethanol (Cellosolve). Both the condenser and the dropping funnel were fitted with calcium chloride drying tubes to insure anhydrous conditions during the reaction. To the contents of the flask was added 23.0 g. (1.0 mole) of metallic sodium in one-gram portions over a period of one

and one-half hours with stirring and with the gentle application of heat. After all the sodium and alcohol had reacted, the solution was cooled to room temperature and 27 ml. (50.60 g., 0.236 mole) of germanium tetrachloride was added dropwise with constant stirring during the course of one hour. An immediate formation and precipitation of sodium chloride was noted upon the addition of the halide. The mixture was then refluxed for sixteen hours to insure completeness of reaction.

The sodium chloride was filtered hot by suction, using Hyflo Supercel as a filter aid, through a large sintered glass funnel equipped with a Glas-Col heating mantle. The residue collected on the filter was thoroughly washed with three 50-ml. portions of 2-ethoxyethanol. The excess alcohol was removed from the filtrate by distillation in vacuo and the yellow liquid residue was fractionally distilled under reduced pressure through a 25-cm. short-path Vigreaux column. There was obtained 104.3 g. (48.6%) of tetrakis(2-ethoxyethoxy) germane, b.p. 126-128°C/0.05 mm; $n^{25}D$ 1.4375.

Anal. Calcd. for $C_{16}H_{36}O_8Ge$: C, 44.79; H, 8.45. Found: C, 44.79; H, 8.59.

E. ATTEMPTED REACTION OF 2-METHOXYETHANOL WITH GERMANIUM TETRACHLORIDE

To 79.01 ml. (76.09 g., 1 mole) of 2-methoxyethanol contained in a 200-ml. three-necked flask equipped as described above for the preparation of the tetrakis(2-alkoxyethoxy) germanes was added dropwise

6.8 ml. (12.9g. 0.059 mole) of germanium tetrachloride. No reaction was observed to occur and after heating for several hours there was no evidence of evolution of hydrogen chloride. The mixture was distilled through a Todd Precise Fractionation and the 2-alkoxyethanol recovered almost quantitatively.

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